Pyrolysis/$(GC)^2$/MS as a Coal Characterization Technique

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INTRODUCTION

With the commercial availability of mini-pyrolyzers coupled with gc/ms intrumentation, many studies(1-7) have been conducted on fossil fuels. However, the studies conducted to date have been limited in two important areas. The first is the lack of a suitable quantification method to describe the patterns of pyrolysates formed and the second is the absence of absolute quantitative yields for the major degradation products. These two features have been included in this present work to demonstrate a generally applicable method for quantifying a wide range of coal pyrolysis products. By employing rapid pyrolysis, that is, a 20°C per millisec heat-up rate with a helium gas sweep, many secondary reactions are avoided. Many of the volatilized coal pyrolysates are swept out of the Pyroprobe hot zone quickly enough so that they still retain much of their structural identity. Analysis of the major chromatographable compounds, therefore, provides some information of the original coal structure.

EXPERIMENTAL

Py/$(GC)^2$/MS System

A Chemical Data Systems Pyroprobe 100 solids pyrolyzer was interfaced to the conventional capillary chromatographic injection port of a Hewlett-Packard 5993 $(GC)^2$/MS/DS system, using glass-lined metal tubing. Alltech 50-meter SCOT SE-30 and OV-17 glass capillary columns with 0.5 mm internal diameters were installed in-line with the pyrolysis interface. Less volatile degradation products were cold trapped on the head of the SE-30 capillary column by maintaining the column oven at either 0° or 10°C. In studies where volatile degradation products were analyzed, volatile degradation product peak widths were minimized by continually sweeping the 5993 injection port with approximately 16 mls/min backflush helium flow, while approximately 4 mls/min helium flow through the OV-17 capillary column was maintained. In addition, the 1.5 mm x 6 cm glass-lined interface line between the pyrolyzer and the capillary column contained several hundred milligrams of Porapak Q Chromatographic support to improve chromatographic separation of the most volatile degradation products.

The pyrolyzer interface and gas chromatographic injection port were maintained at 240°C and 260°C, respectively. A coil type pyrolyzer was used. Solid coal samples were placed in 3 mm i.d. quartz tubes and these tubes inserted in the pyrolysis coil. For the quantitative analysis of volatile degradation products, coal samples were placed on a small amount of quartz wool within the quartz tube and weighed before and after pyrolysis. The coil was heated to 1000°C with a heating ramp of 20°C/msec and maintained at 1000°C for 10 sec.

Previous studies[8,9] reported that a coil temperature of 1000°C results in a sample temperature of approximately 750°C, when similar conditions are used. Degradation products from the inert gas pyrolysis of coal were chromatographed using either a 6°C/min or 8°C/min chromatographic oven heating rate from the starting, subambient temperature, to 250°C.

Quantitative yields of volatile degradation products were determined by using a 0.5 ml gas sampling loop in-line with the pyrolyzer. Characteristic mass responses were determined daily by injecting known volumes of CO_2, CO, CH_4, C_2H_6, C_3H_8, and C_4H_{10} quantitative gas standards, which were supplied by Matheson.

Mass spectral data were stored for later analysis and interpretation using the standard Hewlett-Packard data acquisition system. The mass spectrometer data system was scanned from 35-450 amu for the analysis of less volatile degradation products. Information on volatile degradation products was obtained by scanning the instrument from 10-450 amu. Typical mass spectrometric operating conditions resulted in complete 70 eV mass spectra being obtained every 2 seconds.

Nitrogen compounds were not analyzed in this study. The Illinois No. 6 and Rawhide coals were ground to -80 U.S. mesh and dried at 100°C under vacuum. No further preparation was performed. The compositional analysis of these two coals have been reported[10].

RESULTS AND DISCUSSION

Table I gives a summary of all pyrolysis products identified. A large number of isomers was observed for many methyl-substituted degradation products. Since mass spectra of various isomers are generally very similar, no attempt was made to identify specific isomers using the retention times of known isomers, except for the methyl and dimethyl phenols. In addition, compounds which are identified to contain several methyl groups could also be ethyl or propyl substituted. Therefore, all alkyl-substituted degradation products are listed as isomers under the corresponding methylated compounds.

As can be seen from Figure 1, the total ion chromatogram of the coal pyrolysis products consists of several regions where several degradation products are not completely resolved chromatographically, even though capillary chromatographic separation of the degradation products is used. However, this problem can be minimized if rather than the total ion chromatogram, selected ion chromatograms are used for quantitation. An example of the use of this approach in the quantification of phenols can be seen in Figures 2 and 3. Figure 2 shows the total ion chromatogram, along with molecular ion chromatograms for phenol and methyl phenol isomers produced in the degradation of Illinois No. 6 coal. As can be seen from the comparisons of these molecular ion chromatograms with the total ion chromatogram, only phenol and methyl phenols give peaks at the respective retention times in the ion chromatograms, while the total ion chromatogram yields a large number of overlapping peaks because of the overlapping elution of various degradation products. Figure 3 shows an isometric display of mass spectral data for masses 90-110 at the same retention region shown in Figure 2. Response of masses 94 and 95 are seen to be characteristic of phenol, masses 105 and 106 of trimethylbenzenes and masses 107-109 of methylphenols.

Table I is a summary of the pyrolysates from each coal. The identification of the characteristic mass ions used for quantification of each compound, the characteristic ion percent of total ionization, and the characteristic ion areas, normalized to naphthalene in the Py/$(GC)^2$/MS analysis, are listed for Illinois No. 6 and Rawhide coal degradation products. The values that are given for normalized characteristic ion areas are an average of two Py/$(GC)^2$/MS analyses for each coal sample type and the range of values for each compound in each pyrolysis can be obtained from the variance of each compound listed in the table.

Qualitative differences emphasized by arrows in Figure 1 are also seen in the quantitative comparison of coal degradation products. Good reproducibility, as measured from the variance of each degradation product is obtained for the quantities of all degradation products measured using this technique. For pyrolysates in this volatility range, the quantitative differences observed between the Illinois No. 6 and Rawhide coals are due solely to sulfur-containing heterocyclic compounds. The nonsulfur-containing degradation products are quantitatively similar for the two coals. The one class of compounds which shows the largest variablility in the quantitative determinations of duplicate analyses are the phenols. This is likely due to the fact that these acidic compounds are difficult to chromatograph. While most other degradation product characteristic ion areas vary by 10-15 percent, the phenols typically vary by as much as 30 percent.

High-Volatility Degradation Products

Since a detailed quantitative and qualitative comparison of the relatively nonvolatile degradation products, described above, gives useful information for the characterization of these coals, the same approach was taken to evaluate the differences in the more volatile pyrolysates produced in the inert gas degradation of them. Figure 4 shows the comparison of total ion chromatograms for masses 10-450, produced from the Py/$(GC)^2$/MS analysis of these coals. As in Figures 1 and 2, the numbers listed above each peak refer to peak numbers in Table I and II. Isometric displays of masses 10-46 for Illinois No. 6 and Rawhide coal degradation products are given in Figures 5 and 6. These displays show that methane, carbon monoxide, and carbon dioxide are the degradation products responsible for the major ionization in this mass range. Also, these figures show that the yields of carbon monoxide and carbon dioxide relative to methane are larger in Rawhide coal than in Illinois No. 6. The relatively larger mass 12 shown in Figure 6 is due to C^+ from carbon dioxide and is, therefore, also relatively larger in the mass spectra produced from Rawhide coal degradation products due to the increased yield of this degradation product.

The shoulders on the mass 28 peaks in Figures 5 and 6 show that the normalized area listed for mass 28 as the characteristic ion for carbon monoxide is from more than one compound. The ion chromatograms of masses 25-30 shown in these figures demonstrate that in addition to carbon monoxide, ethane and ethylene are also important degradation products which can produce mass 28. Therefore, unlike other characteristic ion areas listed in Table II, that listed for carbon monoxide is probably due in part to carbon monoxide with some contribution from ethane and ethylene.

To emphasize other degradation products, methane, carbon monoxide, and carbon dioxide degradation products have been excluded from Figure 7 by starting the mass summation range at mass 46. In addition to these three major degradation products, the broad elution of water, which is identified by an asterisk in Figure 3, is also eliminated in Figure 7. The peaks labeled with arrows in Figure 7 are sulfur-containing degradation products and are major pyrolysates which differentiate these two coals (Table II).

Quantitative Yields of Degradation Products

In addition to the normalized yields of products based upon characteristic ion areas, also reported in Tables I and II are the percent of total ionization which these characteristic masses represent in the total mass spectrum of each compound quantified. Since 70 eV electron ionization cross sections of most compounds with masses greater than 70 amu is constant, the absolute naphthalene yield given in Table IV and the compound class yield, relative to naphthalene, given in Table III, can be used to estimate the quantitative yields of all minor degradation products summarized in Table III. If the total relative characteristic ion yields in Table III are normalized to the absolute naphthalene yield of approximately 1 ug/mg of coal, then the sum of all compound classes, in μg/mg of coal would be 27.5 and 25.8 for Illinois No. 6 and Rawhide, respectively. If these yields are added to the major degradation products listed in Table IV, a total of 66.5 and 91.3 ug/mg coal are measured using this analysis technique. Both Illinois No. 6 and Rawhide coals loose approximately 50 percent of their total weight in the 750°C pyrolysis. Therefore, of the weight lost by these two coal samples, approximately 13 and 18 percent is accounted for in the chromatographable degradation products. The data in Table III shows that major differences in the pyrolysates of the two coals appear to result in the formation of large amounts of thiophenes and benzothiophenes.

All other degradation products, with the exception of the carbon oxides are similar for these different ranked coals. The striking similarities of the isomer distributions for the methylthiophenes, dimethylbenzenes, dimethyl thiophenes, methyl phenols, dimethyl phenols, methyl naphthalenes, trimethyl benzenes, dimethyl naphthalenes and methyl dibenzofurans, produced from both coals indicate that the organic structures producing these degradation products in the two coals are very similar.

One additional important conclusion which may be drawn concerning the organic structure of coal is reflected in the complete absence of substituted furans. No oxygen heterocyclic degradation products were observed from either the eastern or western coals which were alkylated furans. However, about one-half of the sulfur-containing organic degradation products are the sulfur-containing analogue of furan, i.e., alkylated thiophenes. While it is possible that the alkylated phenol degradation products could be a result of furan degradation, the complete absence of alkyl furans may imply that only benzofuran structures are the important heterocyclic oxygen-containing structures present in the primary coal structure.

To measure absolute yields for the major volatile degradation products listed in Table II, a calibrated gas standard was used to calibrate the $(GC)^2/MS$ analysis system. Weighed quantities of coals in the low milligram range were pyrolyzed and the characteristic ion areas produced from the analysis of the pyrolysates were compared to this quantitative gas standard. Approximately 50 percent of the coal sample weight was lost when heated under the conditions listed above. Table IV gives the absolute yields of methane, carbon monoxide, carbon dioxide, ethane, carbonyl sulfide, and naphthalene determined in this manner.

As can be seen from Table IV, a major difference observed in the major degradation products of these two coals is in the carbon dioxide yields. From studies reported by Schafer[11,12] on the pyrolytic yields of carbon dioxide produced from brown coals at various degradation temperatures, complete decarboxylation of the coals yielding carbon dioxide was observed at temperatures greater than 700°C. In addition, he deduced that carbon monoxide, which is also produced with different yields from these two coals, is due to phenolic groups present in the coal. If this is the case then from the absolute quantities of the major degradation products shown in Table IV, it can be seen that not only does Rawhide contain approximately 3 times more carboxylic acid groups than Illinois No. 6, but also in Rawhide coal, these groups comprise approximately 3.7 percent by weight, of the total coal sample.

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Table 1. Characteristic Ion Areas Measured for the Major Inert Gas Degradation Products with Volatilities Less Than or Equal to Toluene Obtained from the Py/(GC)^2/MS Analysis of Illinois No. 6 and Rawhide Untreated Coals.

Peak Number	Retention Time (Min)	Degradation Product	Characteristic Masses Used for Quantitation	Percent of Total Ionization	Illinois No. 6	Rawhide
1	7.8	Toluene	91 - 93	60.5	2.91 ± 0.48	3.16 ± 0.53
		Methyl Thiophenes	97 - 99			
2	7.9	Isomer #1			0.341 ± 0.039	0.062 ± 0.015
3	8.2	Isomer #2		66.1	0.209 ± 0.016	0.035 ± 0.008
		Dimethyl Benzenes	91-92, 105-106			
4	11.7	Isomer #1			0.193 ± 0.020	0.259 ± 0.029
5	11.9	Isomer #2		55.3	1.063 ± 0.16	1.175 ± 0.228
6	12.5	Isomer #3		55.7	0.396 ± 0.062	0.486 ± 0.096
7	12.4	Styrene	77-79, 102-105	61.5	0.667 ± 0.023	0.718 ± 0.100
8	15.0	Phenol	65-66, 94-95	54.7	1.139 ± 0.295	1.87 ± 0.65
		Dimethyl Thiophenes	111 - 113			
9	11.8	Isomer #1			0.108 ± 0.016	0.012 ± 0.007
10	12.1	Isomer #2		39.0	0.130 ± 0.008	0.017 ± 0.007
11	12.3	Isomer #3			0.085 ± 0.001	0.011 ± 0.005
12	15.1	Benzofuran and methyl styrene	89-90, 117-119	50.5	0.562 ± 0.066	0.707 ± 0.117
13	16.1	Indane	115-119		0.061 ± 0.012	0.052 ± 0.009
14	16.3	Indene	115-117	65.5	0.767 ± 0.115	0.606 ± 0.106
		Methyl Phenols	77-81, 107-109			
15	16.5	Isomer #1		58.6	0.673 ± 0.26	0.642 ± 0.333
16	16.9	Isomer #2		67.5	2.336 ± 0.76	1.923 ± 0.959
17	17.4	Methyl benzofuran	102-105, 131-133	45.6	0.374 ± 0.021	0.301 ± 0.047
18	18.3	Methyl Indene	115, 127-131	57.9	0.345 ± 0.121	0.299 ± 0.121
19	18.4	Dihydronaphthalene	115, 127-131	56.1	0.455 ± 0.140	0.425 ± 0.144
20	19.1	Naphthalene	126-129	62.0	1.000	1.000
21	19.2	Benzothiophene	134-136	53.9	0.229 ± 0.010	0.057 ± 0.032
		Dimethyl phenols	107-108, 121-123			
22	18.3	Isomer #1		51.5	0.717 ± 0.304	0.390 ± 0.236
23	18.8	Isomer #2		50.0	0.641 ± 0.246	0.434 ± 0.242
24	19.6	Dimethyl benzofuran	145-147		0.120 ± 0.027	0.148 ± 0.054
		Methyl Naphthalene	115, 139-143			
25	21.1	Isomer #1		71.1	0.768 ± 0.030	0.651 ± 0.013
26	21.4	Isomer #2		67.3	0.522 ± 0.039	0.512 ± 0.036
27	22.4	Acenaphthene or biphenyl	151-155	62.6	0.140 ± 0.006	0.117 ± 0.007
28	23.5	Acenaphthalene or biphenylene	150-153	68.6	0.413 ± 0.010	0.296 ± 0.031
29	24.5	Dibenzofuran	139, 168-170	69.8	0.157 ± 0.002	0.191 ± 0.012
		Trimethyl benzenes	105-106, 120			
30	14.6	Isomer #1			0.171 ± 0.011	0.236 ± 0.023
31	14.7	Isomer #2		61.9	0.082 ± 0.006	0.077 ± 0.019
32	14.9	Isomer #3			0.044 ± 0.002	0.064 ± 0.006
33	15.2	Isomer #4			0.255 ± 0.031	0.251 ± 0.053
34	15.8	Isomer #5			0.088 ± 0.012	0.188 ± 0.028
		Dimethyl naphthalenes	141, 155-157			
35	22.8	Isomer #1			0.167 ± 0.021	0.116 ± 0.003
36	23.2	Isomer #2 and 3			0.372 ± 0.068	0.345 ± 0.024
37	23.5	Isomer #4			0.177 ± 0.010	0.119 ± 0.007
38	23.7	Isomer #5			0.062 ± 0.012	0.066 ± 0.006

Continued

Table 1. Continued

Peak Number	Retention Time (Min)	Degradation Product	Characteristic Masses Used for Quantitation	Percent of Total Ionization	Illinois No. 6	Rawhide
		Methyl dibenzofurans	181–184			
39	26.0	Isomer #1		53.9	0.092 ± 0.005	0.083 ± 0.001
40	26.3	Isomer #2		63.5	).203 ± 0.006	0.131 ± 0.003
41	28.2	Phenanthrene	176–179	65.6	0.397 ± 0.043	0.258 ± 0.051
42	28.3	Anthracene	176–179	68.6	0.141 ± 0.014	0.087 ± 0.017
43	25.5	Fluorene	163–167	78.9	0.344 ± 0.006	0.286 ± 0.017
44	9.7	C_8-alkene	41-43, 55-57		0.105	0.229 ± 0.064
45	10.0	C_8-alkane	41-43, 55-57		0.099	0.128 ± 0.007
46	12.8	C_9-alkene	41-43, 55-57	73.1	0.091 ± 0.006	0.214 ± 0.065
47	13.2	C_9-alkane	41-43, 55-57	55.7	0.088 ± 0.011	0.127 ± 0.009
48	15.4	C_{10}-alkene	41-43, 55-57		0.088 ± 0.0010	0.235 ± 0.070
49	15.7	C_{10}-alkane	41-43, 55-57		0.073 ± 0.015	0.119 ± 0.004
50	17.5	C_{11}-alkene	41-43, 55-57		0.075 ± 0.002	0.187 ± 0.042
51	17.7	C_{11}-alkane	41-43, 55-57		0.068 ± 0.004	0.116 ± 0.000
52	19.5	C_{12}-alkene	41-43, 55-57		0.056 ± 0.002	0.152 ± 0.033
53	19.7	C_{12}-alkane	41-43, 55-57		0.094 ± 0.033	0.106 ± 0.005
		Methyl benzothiophenes	147–148			
54	20.8	Isomer #1		48.8	0.060 ± 0.001	0.010 ± 0.004
55	21.0	Isomer #2			0.125 ± 0.007	0.018 ± 0.007
56	21.1	Isomer #3		41.7	0.094 ± 0.020	0.018 ± 0.005
57	21.2	Isomer #4		55.5	0.100 ± 0.004	0.016 ± 0.005
58	21.4	Isomer #5			0.017 ± 0.006	0.003
		Dimethyl benzothiophenes	161–163			
59	22.6	Isomer #1		58.0	0.061 ± 0.009	0.0038
60	22.7	Isomer #2			0.024 ± 0.005	0.0164
61	22.8	Isomer #3			0.100 ± 0.007	0.0066
62	22.9	Isomer #4			0.050 ± 0.001	0.0027
63	23.1	Isomer #5			0.039 ± 0.005	0.0044
64	23.2	Isomer #6			0.022 ± 0.003	0.0091
65	27.8	Dibenzothiophene	184–186	60.3	0.091 ± 0.003	--
		Trimethyl thiophenes	111, 125–126			
66	14.9	Isomer #1			0.094 ± 0.037	--
67	15.6	Isomer #2			0.034 ± 0.012	--

Table 2. Characteristic Ion Areas Measured for the Major Inert Gas Degradation Products with Volatilities Greater than Toluene Obtained from the $Py/(GC)^2/MS$ Analysis of Illinois No. 6, and Rowhide Utreated Coals.

Peak Number	Retention Time ** (Min)	Degradation Product	Characteristic Masses Used for Quantitation	Percent of Total Ionization	Illinois No. 6	Rowhide
68	4.9	Methane	15-16	81.1	38.8 ± 1.6	48.5 ± 14.8
69	4.9	Carbon Monoxide	28	>90.0	25.2 ± 2.4	63.2 ± 12.0
70	5.1	Carbon Dioxide	44	60.2	7.75 ± 1.06	32.7 ± 9.1
71	-	Ethylene	No Unique Masses	-	-	-
72	5.0	Ethane	30	*13.5	0.78 ± 0.05	0.60 ± 0.13
73	5.2	Propene	42	*19.7	0.99 ± 0.00	1.03 ± 0.07
74	-	Propane	No Unique Masses	-	-	-
75	5.7	Butene	55-56	*20.0	0.60 ± 0.02	0.58 ± 0.04
76	6.0	Butadiene	53-54	*39.1	0.55 ± 0.08	0.56 ± 0.08
77	5.2	COS	60	44.5	0.46 ± 0.06	0.09 ± 0.01
78	5.2	H_2S	34	*51.8	0.56 ± 0.20	-
		Methyl butadienes	67-68	*34.7		
79	8.9	Isomer #1			0.11	0.051
80	9.1	Isomer #2			0.19 ± 0.03	0.10 ± 0.02
81	9.3	Cyclopentadiene	65-66	*57.4	0.66 ± 0.04	0.64 ± 0.04
82	12.5	Cyclohexadiene (2 isomers)	77-80	*73.9	0.45 ± 0.05	0.34 ± 0.01
83	13.6	Benzene	77-79	*63.6	2.34 ± 0.01	2.62 ± 0.08
84	9.3	CS_2	76,32	*78.7	0.38 ± 0.08	--
85	14.5	Thiophene	45,58,84	60.5	0.32 ± 0.02	--

* Percent of Total Ionization obtained from Reference 21.

** Coal pyrolysis occurs at 2.0 minutes.

Table 3. Comparison of classes of pyrolysates listed in Tables 1 and 2 in the inert gas degradation of untreated coals.

Compound class	Characteristic Ion Yields (Relative to Naphthalene) Illinois No. 6	Rawhide
alkyl benzenes*	8.21	9.23
polynuclear aromatic hydrocarbons	6.13	5.24
benzofurans*	0.95	0.85
phenols	5.51	5.26
thiophenes	1.32	0.14
benzothiophenes	1.01	0.17
alkenes (C_8-C_{12})	0.42	0.60
alkanes (C_8-C_{12})	0.42	1.02
alkenes (C_3-C_6)	3.55	3.30

*Exclusive of benzofuran and methyl styrene

Table 4. Quantatative yield of major volatile degradation products formed in the inert gas degradation of untreated coals.

Degradation Product	Yield (microgram/milligram) Illinois No. 6	Rawhide
Methane	11.9 ± 0.3	10.4 ± 1.0
Carbon Monoxide	8.0 ± 0.7	14.6 ± 3.1
Carbon Dioxide	12.4 ± 1.5	36.6 ± 4.6
Ethane	4.2 ± 0.2	2.4 ± 0.5
Carbonyl Sulfide	2.5 ± 0.2	0.3 ± 0.0
Naphthalene	1.2 ± 0.0	0.9 ± 0.4

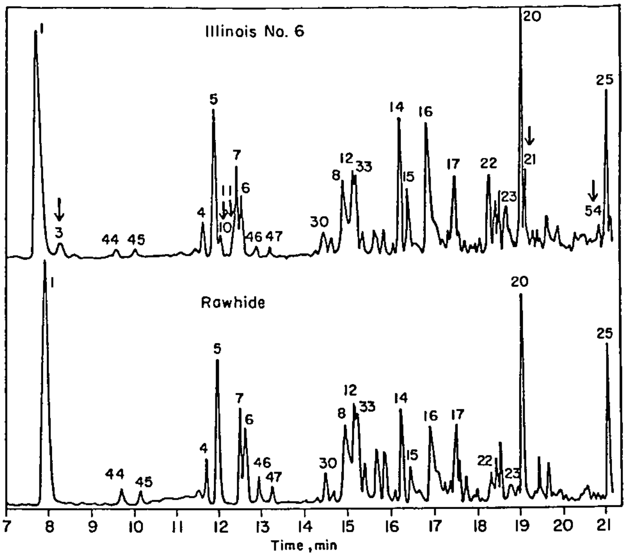

Figure 1. Comparison of pyrolysates from untreated coals. Arrows indicate significant visual differences between the two samples.

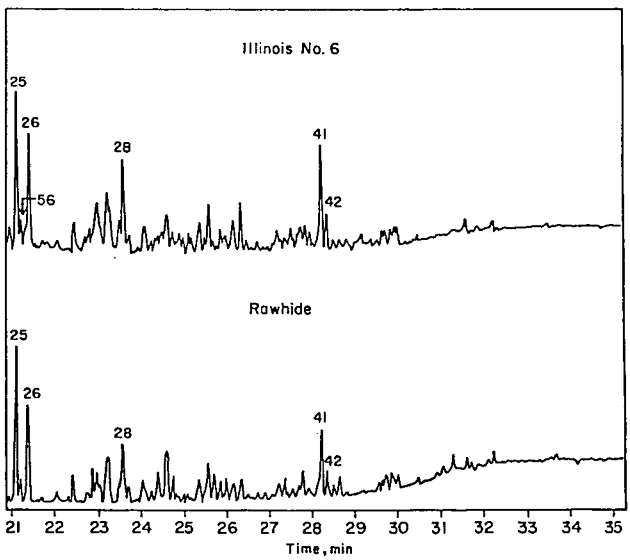

Figure 1. (continued)

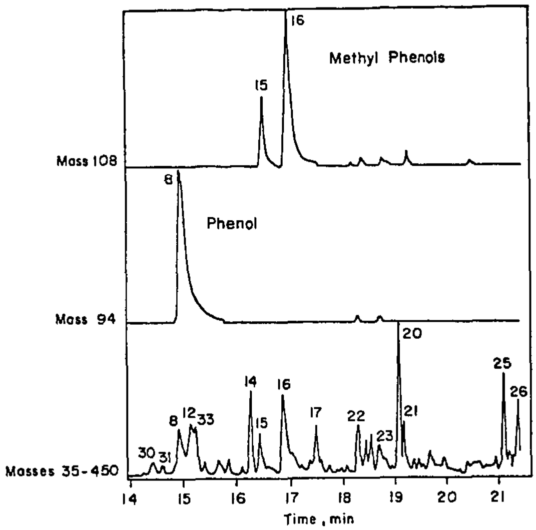

Figure 2. Comparison of Masses 35-450 total ion chromatogram and characteristic ion chromatograms used for the quantitation of phenol and methyl phenol present as pyrolysates of Illinois No. 6 coal.

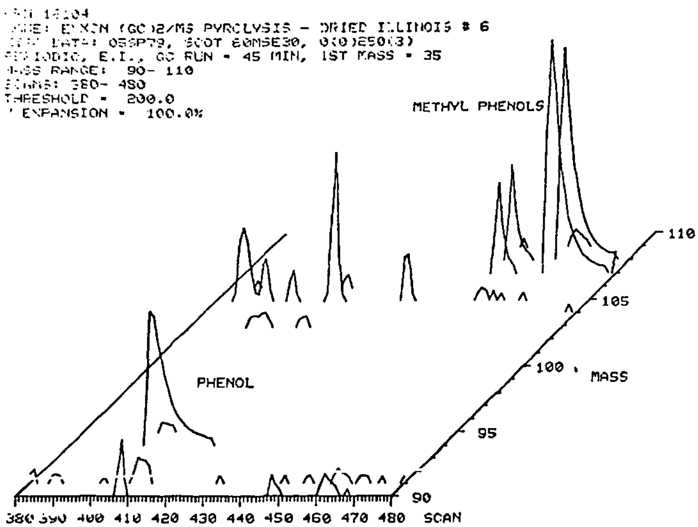

Figure 3. Isometric display of Masses 90-110 in the retention time region of phenol and methyl phenol, produced in the inert gas degradation of Illinois No. 6 coal.

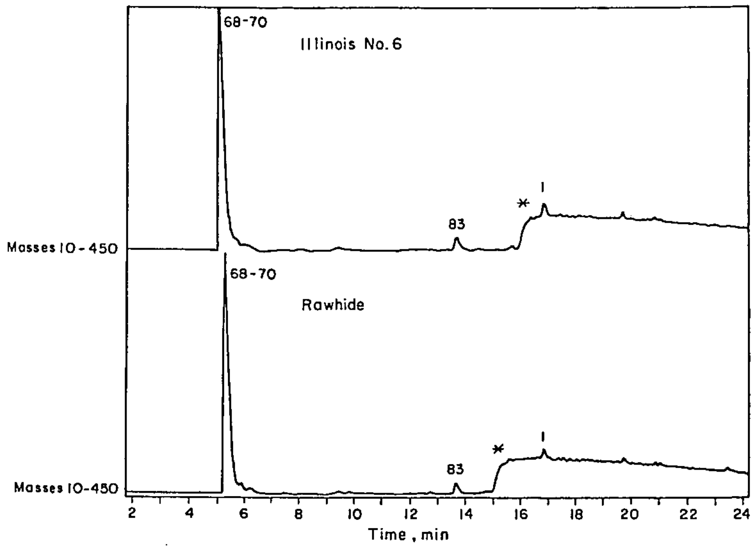

Figure 4. Comparison of Masses 10-450 total ion chromatograms of volatile pyrolysates from untreated coals.

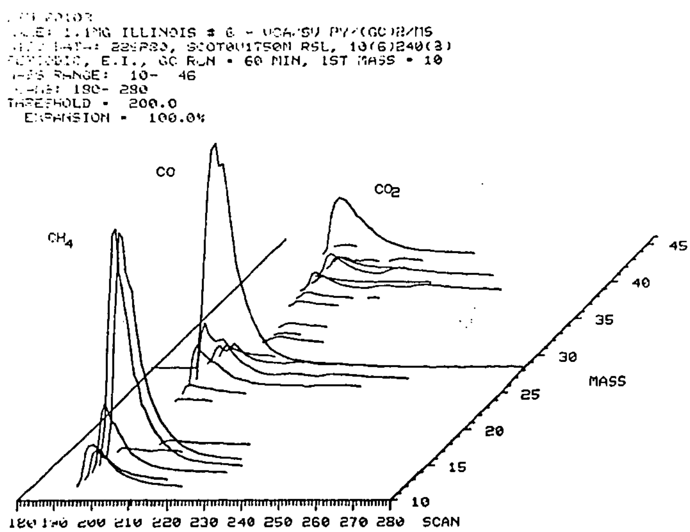

Figure 5. Isometric display of Masses 10-46 in the retention time region of volatile pyrolysates produced in the inert gas degradation of Illinois No. 6 coal.

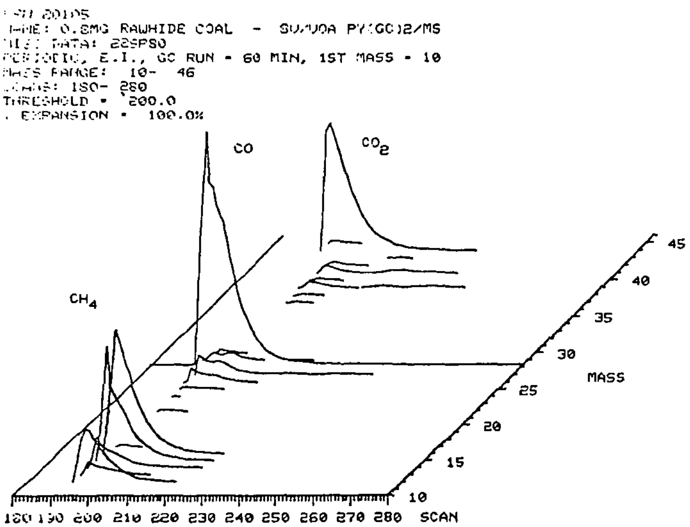

Figure 6. Isometric display of Masses 10-46 in the retention time region of volatile pyrolysates produced in the inert gas degradation of Rawhide coal.

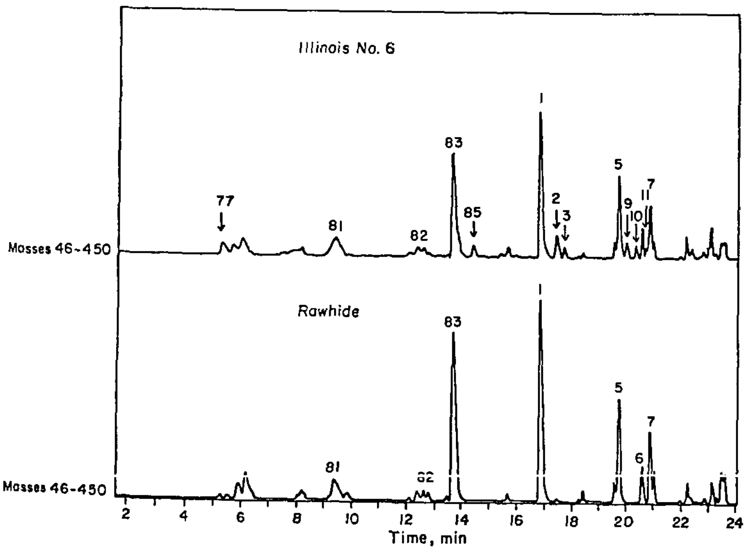

Figure 7. Comparison of Masses 46-450 total ion chromatograms of untreated coals. *Arrows indicate significant visual differences between the two samples.*